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EXPLOSION HAZARDS ASSOCIATED WITH PROPELLANTS AND FUEL OIL ADDITIVES

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MICROMEDIA

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by

D.E.G. Jones* and K.K. Feng*

ABSTRACT

Research on energetic material compositions may pose certain hazards to the personnel doing experimental studies. It is therefore important that some preliminary investigation of these hazards be carried out. This report describes such an analysis for a propellant composition and a low grade fuel composition containing an energetic material as an additive. Results of thermohydrodynamic calculations are described for both of these compositions.

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Keywords:
Explosion hazards, propellants, fuel oil additives, thermohydrodynamic calculations

RISQUES D'EXPLOSION ASSOCIÉS AUX PROPERGOLS ET AUX ADDITIFS POUR HUILE COMBUSTIBLE

par

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RÉSUMÉ

La recherche sur les composés de matériaux énergétiques présente des risques pour le personnel préposé à la recherche expérimentale. Par conséquent, il est important de réaliser une étude préliminaire des dangers liés aux explosions. Le rapport comprend la description d'une analyse de ce genre portant sur la composition des propergols et d'un composé combustible à faible teneur contenant un matériau énergétique comme additif. Les résultats des calculs thermohydrodynamiques pour ces deux composés sont présentés dans le rapport.

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Mots clés :

Dangers liées aux explosions; propergols; additifs pour l'huile combustible; calculs thermohydrodynamiques.

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INTRODUCTION

This study was initiated at the request of the Mechanical Engineering Department of the Royal Military College (RMC) in Kingston. The contact was made as a result of one of the authors (D.E.G. Jones) attending the spring meeting of the Combustion Institute, 1989.

RMC is conducting research on the combustion phenomena of propellants and low grade fuels. They are concerned about the explosion hazards associated with the presence of certain oxidizers in the propellant and oxidizers/free radical generators (OFRG) in the low grade fuels.

The propellant is a potassium chlorate based product being used by Defence Research Establishment Valcartier (DREV). The composition of the propellant was supplied by RMC.

The OFRG in the low grade fuels is intended to be used as an additive for the purpose of enhancing the performance of the low grade fuels. RMC suggested the following conditions as a starting point for the determinations: (i) dodecane be used to simulate the low grade fuel (ii) the additive be used as a one molar aqueous solution and (iii) ten mass percent of additive solution be used.

No specific fuel oil additive had been chosen by RMC so that efficiency of the additive in its intended function is a clear consideration. A number of possible additives were suggested by RMC, however, some of these materials were eliminated because of one or more of the following reasons: (i) low solubility in water (ii) extreme toxicity and (iii) environmental hazards.

PROCEDURE

Thermohydrodynamic calculations may be used to assess the explosion and detonation parameters possible from a specific composition. An outline of the theory on which such calculations are based is given in (1). In this theory, detonation is assumed to be "ideal" in the sense that all the materials in the composition are reacted. Further, detonation is considered to occur under C-J (2) conditions. Among the important limitations of this treatment are (i) the assumption of equilibrium between the unreacted and reacted composition and (ii) independence of the physical properties of the composition other than density.

This theory is embodied in the computer code, TIGER (3) and this code has been used in the calculations of this report. TIGER requires a library of data which includes the chemical elements encompassed by the composition and a compendium of a number of possible detonation products along with assorted thermodynamic and molecular properties of these products. Further, as input to the code the following information is required:

(i) the chemical formula and enthalpy of formation at 298 K of each component of the composition,

(ii) the weight (or mole) percent of each component of the composition,

(ii) the density of the composition, and

(iv) a selected equation of state (or potential energy function) to represent each of the possible gaseous detonation products.

PROPELLANT

The properties of the propellant are listed in Table 1. In the calculations for the propellant, $KClO_3$ was replaced by $NaClO_3$ since K is not included in the library of data. Since both Na and K are in Group I of the Periodic Table, it is expected that the chemical properties of $KClO_3$ will be similar. Further, the oxygen balance (OB) is 45.1% for $NaClO_3$ compared to 39.2% for $KClO_3$, assuming combustion to produce alkali metal chloride and oxygen.

$\Delta_f H°$ (298 K) for polyvinylacetate was estimated by a thermodynamic group contribution method (4). Explosion and detonation calculations using TIGER were done for the propellant compositions given in Table 2.

TABLE 1

Properties of Components of Propellant Composition

Material	Chemical Formula	Mass %	$-\Delta_f H°(298\ K)$ /kJ mol^{-1}
A	$NaClO_3$	20-30	358.7
B	$C_{12}H_{22}O_{11}$ (sucrose)	20	2226.
C	Na_2CO_3	5-10	1130.
D	$(C_4H_6O_2)n$ (polyvinylacetate)	40-55	336.9

$V = 0.714\ cm^2\ g^{-1}$

TABLE 2

Propellant Compositions for Thermohydrodynamic Calculations

Propellant Composition	Component Mass %		
	A	B	C
1	20	20	5
2	30	20	5
3	20	20	10
4	30	20	10

FUEL OIL ADDITIVES

The properties of the fuel oil components are listed in Tables 3 and 4. The mass percent of additive A in Table 4 is calculated assuming the aqueous solution containing A is 10.0 mass percent.

Many of the OFRG are those commonly used in energetic material compositions.

Calculations using TIGER were done for compositions containing A both in the condensed state and in the vapour state ie. at low density, in the presence of air. The latter conditions attempt to reproduce the conditions under which the fuel is sprayed into an ignition system.

TABLE 3

Properties of Additives and Other Components
in Low Grade Fuels

Name	Chemical Formula	$-\Delta_f H°(298\ K)$ /kJ mol^{-1}	Density /g cm^{-3}
ammonium nitrate	$H_4N_2O_3$	366	1.73
ammonium perchlorate	H_4NO_4Cl	295	1.95
hydrazonium nitrate	$H_5N_3O_3$	252	1.64
ammonium azide	H_4N_4	-115	1.35
hydrogen peroxide	H_2O_2	188	1.40
methyl ammonium nitrate	$CH_6N_2O_3$	354	1.42
dimethyl ammonium nitrate	$C_2H_8N_2O_3$	350	1.42
nimethyl ammonium nitrate	$C_3H_{10}N_2O_3$	344	1.42
tetramethyl ammonium nitrate	$C_4H_{12}N_2O_3$	346	1.50
ethanol amine dinitrate	$C_2H_7N_3O_6$	628	1.53
ethylene diamine dinitrate	$C_2H_{10}N_4O_6$	564	1.60
urea nitrate	$CH_5N_3O_4$	564	1.59
formaldehyde	CH_2O	117	0.82
acetaldehyde	C_2H_4O	192	0.78
propyl nitrate	$C_3H_7NO_3$	222	1.04
dodecane (fuel)	$C_{12}H_{26}$	351	0.75
water	H_2O	286	1.00

TABLE 4

Concentration of Additives and Other Components
in Low Grade Fuels

Chemical Formula	**Molar Mass /g mol^{-1}**	**Mass %**
Additives A		
$H_4N_2O_3$	80.05	0.774
H_4NO_4Cl	117.49	1.11
$H_5N_3O_3$	95.07	0.917
H_4N_4	60.07	0.592
H_2O_2	32.02	0.337
$CH_6N_2O_3$	94.08	0.915
$C_2H_8N_2O_3$	108.11	1.04
$C_3H_{10}N_2O_3$	122.13	1.18
$C_4H_{12}N_2O_3$	136.16	1.30
$C_2H_7N_3O_6$	169.11	1.60
$C_2H_{10}N_4O_6$	186.14	2.71
$CH_5N_3O_4$	123.08	1.18
CH_2O	30.03	0.303
C_2H_4O	44.05	0.445
$C_3H_7NO_3$	105.10	1.05
Fuel		
$C_{12}H_{26}$	170.33	90.0
Solvent for A		
H_2O	18.02	10.0 - %A

RESULTS

PROPELLANT

Results for the TIGER code calculations of the explosion and detonation properties of the various propellant compositions are listed in Table 5. Table 6 gives the concentration of detonation products per kilogram of propellant composition. Figure 1 shows the behaviour of the detonation pressure and temperature as the detonation products expand isentropically. The corresponding effect on the concentration of the detonation products is depicted in Figure 2.

The results of these calculations indicate that there is a serious hazard should explosion or detonation take place. The high pressures ($\sim$100 kbar) and temperatures ($>$2400 K) produced from detonating these compositions warrant care in conducting combustion experiments on such materials.

Further, these compositions produce significant proportions of CO, which is toxic. Moreover, the concentration of CO increases significantly on expansion as do the concentrations of CH_4 and H_2. Finally, the amount of C(s) produced indicates that the propellant is not oxygen balanced ie. the composition is not adjusted to effectively "burn" all the "fuel" components. Since the OB of $KClO_3$ is less positive than that of $NaClO_3$, it is evident that these properties will be even more pronounced for the actual propellant composition.

Figure 1

Detonation Properties of Propellant Composition 1

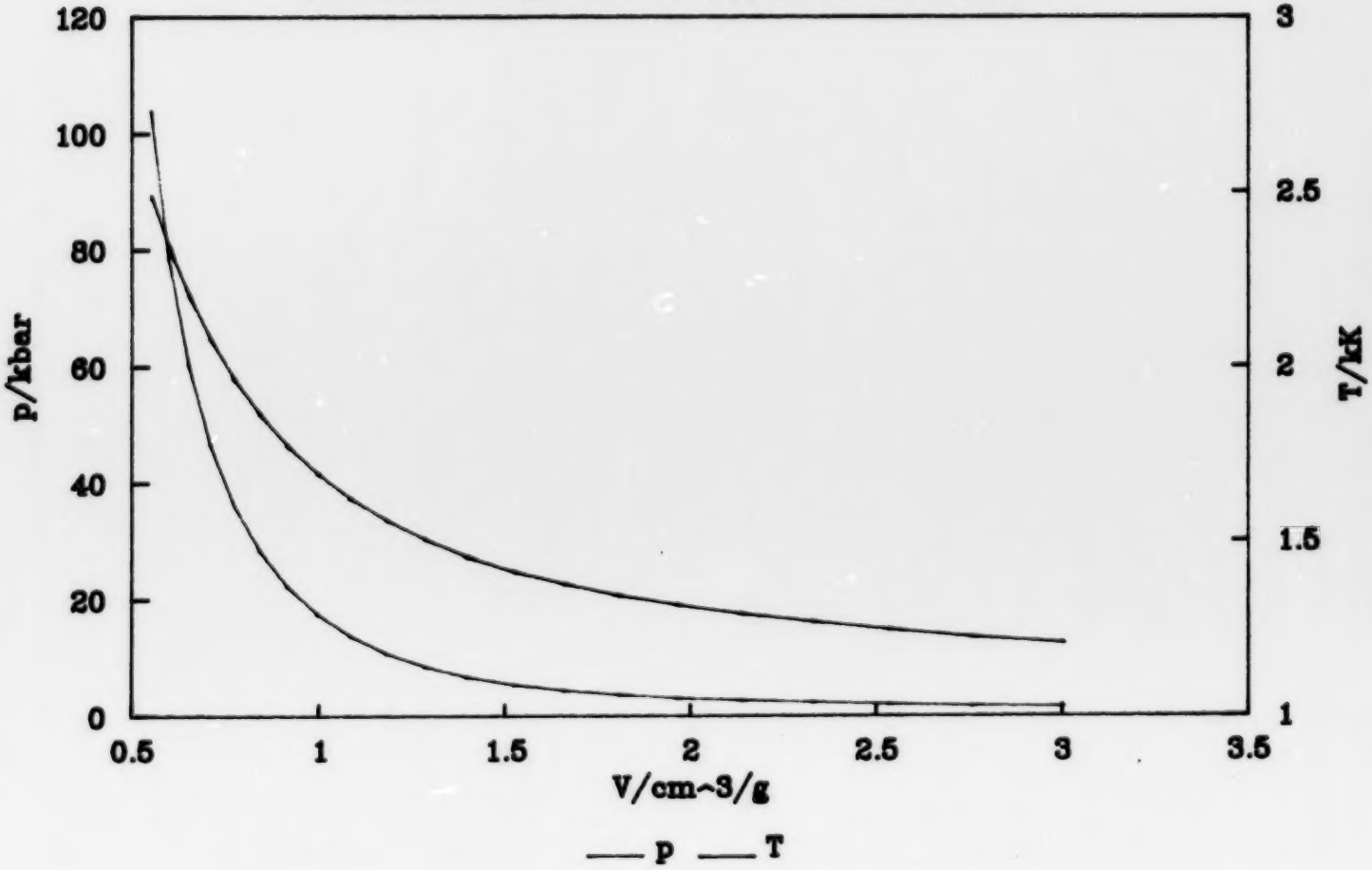
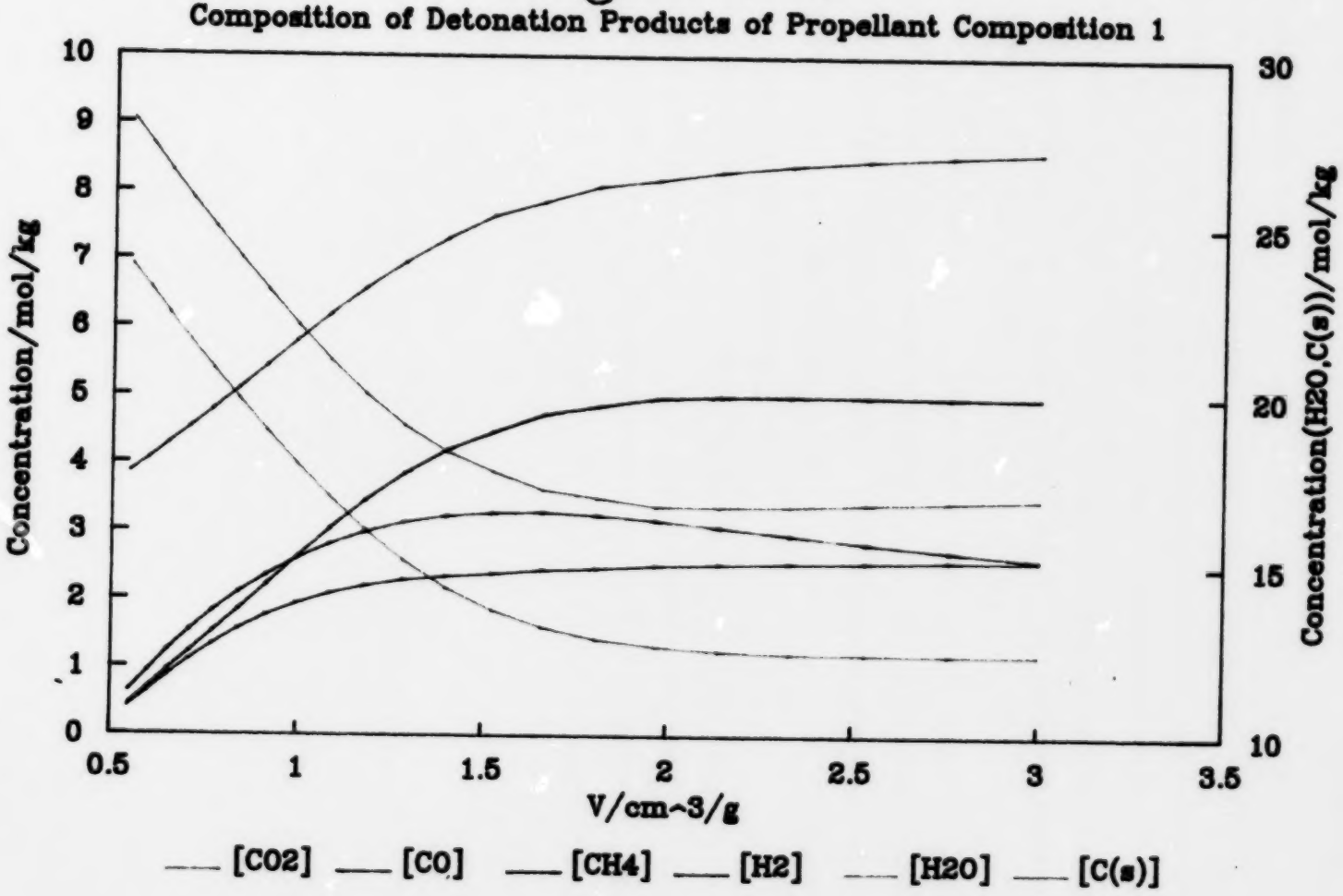


Figure 2


Composition of Detonation Products of Propellant Composition 1
Concentration/mol/kg
Concentration(H2O,C(s))/mol/kg
V/cm~3/g
0
1
2
3
4
5
6
7
8
9
10
0.5
1
1.5
2
2.5
3
3.5
10
15
20
25
30
[CO2]
[CO]
[CH4]
[H2]
[H2O]
[C(s)]

FUEL OIL ADDITIVES

At the conditions suggested by RMC, TIGER calculations yielded virtually identical results for every additive, respectively, in the condensed and vapour state. This is not surprising since the proportion of additive is quite small. The results of these calculations are summarized in Table 7. Clearly, these results indicate that there is little hazard arising from the possible detonation of these compositions, especially considering the low detonation temperatures determined.

These conditions represent a poor choice in terms of efficiency since they are very "fuel rich", even in the vapour state, assuming 80% air. Further, many of the OFRG provide an additional source of fuel. Increasing the amount of OFRG in that case simply adds more fuel without significantly increasing the performance. Moreover, additional OFRG is limited by (i) its solubility in water and (ii) the cost of the OFRG.

It may be preferable to avoid using an aqueous solution of OFRG but it is obviously advantageous to use an OFRG which is liquid at room temperature. Hydrogen peroxide is a prime example of such an OFRG. Further, hydrogen peroxide does not provide a source of additional C containing fuel. Table 8 summarizes the detonation parameters obtained using 30 mass % hydrogen peroxide.

TABLE 7

Results of C-J Calculations with Various Additives
in Low Grade Fuels

				Concentration/mol kg^{-1}							
	p/bar	$V/cm^3\ g^{-1}$	T/kK	N_2	H_2	CO	CH_4	CO_2	H_2O	NH_3	C(s)
Vapour state $V_o=1000\ cm^3\ g^{-1}$ 80% air	8.0	580	1.19	22.9	13.1	9.7	0.5	0.4	0.7	.01	2.2
Condensed state $V_o=1\ cm^3\ g^{-1}$	$101x10^3$	0.84	0.51	----	.003	----	34.2	----	5.2	0.3	29.3

TABLE 8

Detonation Parameters for Low Grade Fuel
Containing Hydrogen Peroxide

	p/bar		$V/cm^3\ g^{-1}$		T/kK	
Composition	10^{-3} x condensed	vapour	condensed	vapour	condensed	vapour
30% H_2O_2	82.9	8.7	0.807	562	1.53	1.01
50% air	52.2	8.8	0.733	568	1.94	1.11
80% air	59.0	11.3	0.746	582	2.23	1.76

CONCLUSIONS

TIGER code calculations indicate that the propellant composition being tested by RMC may pose an explosion hazard. The results indicate that further tests, such as thermal analysis and impact tests, may be warranted.

For the fuel oil compositions, it appears that there is little hazard arising from using these compositions under the conditions suggested by RMC. However, it is also apparent that such conditions neither allow selection of a preferred OFRG nor do they provide the most effective composition in terms of enhancing the performance of the low grade fuels. Preliminary calculations suggest the use of hydrogen peroxide, in the absence of water, is advantageous for enhancing performance without providing significant explosion hazard. Hydrogen peroxide has the additional advantage of being environmentally clean by comparison with many of the possible OFRG tested. Finally, economic considerations will clearly influence both the choice of OFRG and, additionally, the proportion of OFRG used with the low grade fuel.

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